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A key piece of the ferroelectric hafnia puzzle

Theoretical calculations reveal flat phonon bands that enable homogeneous dipole ordering

By Beatriz Noheda^{1,2} and Jorge Íñiguez^{3,4}

The ferroelectrics community is witnessing one of those moments in which serendipity changes the course of science. The story of ferroelectric hafnia (HfO_2) is a bit like that of Cinderella. Like the girl who was not invited to the ball, nanoscale hafnia (HfO_2), by conventional theory, should not be a ferroelectric, a material that has a spontaneous polarization, despite the experimental evidence for this response. On page xxx of this issue, Lee *et al.* (1) bring us closer to a real-life fairytale ending with their theoretical calculations which show that nanoscale hafnia becomes a ferroelectric through a different mechanism. Polarization is not associated with heterogeneous domains of ferroelectric order but with flat polar phonon bands that allow for homogenous polar ordering of electric dipoles.

The story starts with research that began 2006 but not published until 2011 (2). Scientists fabricating silicon transistors with HfO_2 -based insulating layers [as meant? They are Si transistors] spent several years trying to explain the origin of a strange peak observed in the capacitance-voltage characteristics. The peak looked very much like the ones observed in ferroelectrics when an applied electric field switches that direction of the spontaneous polarization. This feature has made of ferroelectrics one of the oldest nonvolatile semiconductor memory types (3).

The problem is that no ferroelectric phases had ever been reported in hafnia, a refractory material with a long history of research (4), and because these hafnia layers were only a few nanometers thick. Ferroelectricity is not expected at the nanoscale because it is a cooperative phenomenon. The local dipoles in ferroelectric materials,

which result from the relative displacement of positive and negative ions, interact electrically with the dipoles of the neighboring cells and have a tendency to align collectively in the same direction, akin to what happens in a ferromagnet with the electron spins. The collective ordering leads to a spontaneous polarization. However, when the dimensions of the ferroelectric sample are small, as needed in microelectronics, a substantial number of dipoles lie on its surface. The stabilization of ferroelectric phase is hampered by the energy cost of the depolarizing electric field that such dipoles create inside and outside the ferroelectric material, as dictated by Maxwell's equations.

In nature, this electrostatic penalty is reduced by domain formation, in which regions with alternating polarization (up and down) form in the sample. In theory, compensation of the dipolar surface charges can also be achieved by sandwiching the ferroelectric in between two metallic electrodes. The free carriers of the metal should screen the polarization charges and eliminate the depolarizing field and avoiding the need to form domains. In practice, this approach does not work perfectly with real metals and screening is not complete (5). How to work around this issue has been one of the main research focusses of the ferroelectrics community for more than 30 years, driven by the vision of a ferroelectric nonvolatile memories that would be faster, denser, and less power consuming than their magnetic counterparts (6).

Thus, even when the paper reported on ferroelectric hafnia was published (2), the ferroelectrics community largely dismissed this result as an artifact, assuming that a material that is not polar in bulk would not become polar at the nanoscale. Moreover, at the nanoscale, it is hard to distinguish ferroelectric switching peaks from the voltammetry characteristics that could arise from electrochemical reactions at interfaces (7). However, after many subsequent studies from several groups (8), the evidence for robust switching became difficult to ignore. The current consensus is that ferroelectric-like switching in hafnia-based ferroelectrics

does exist, but its origin still highly debated. Only one or two reports have shown a ferroelectric phase transition in this material (9, 10). In addition, switching requires large applied fields and does not seem to proceed as in other ferroelectrics through movement of domain walls (11).

How hafnia becomes ferroelectric at the nanoscale and how it screens polarization charges at surfaces are the main questions to resolve. The former has been explained by a combination of effects (surface-energy, ordered dopants, and oxygen vacancies) that favor the occurrence of the polar phase (3, 7). The latter could be explained by the much lower dielectric permittivity of hafnia compared with other ferroelectrics, but why is it so low?

Theoretical calculations by Lee *et al.*, now show that ferroelectricity in hafnia is of a different type. The polar features of hafnia are associated with a nearly flat phonon band (similar frequency of the different vibrations along the band). Thus, a homogenous polar order, in which all electric dipoles align parallel as in a regular 3D ferroelectric phase, is as likely as any longitudinally-modulated inhomogeneous order in which an arbitrary sequence of ferroelectric domains are separated by 180° domain walls. Put differently, the domain walls in hafnia have essentially zero energy cost and a negligible width.

This situation, reminiscent of the effect called pressure-induced amorphization (12), has two important consequences. First, hafnia has essentially two-dimensional (2D) polar instabilities, meaning that a polar 2D plane (polarization within the plane) can in principle appear by itself, even if the rest of the material remains nonpolar. Interestingly, the polarization of such 2D layers has a very small electrostatic penalty (depolarizing field) associated to it, much smaller than that for 3D polar order, which helps explain why ferroelectricity occurs in hafnia [only?] at the nanoscale.

Second, the 2D polar layers are all but decoupled from each other, so in hafnia, the switching of one domain has no effect on its surrounding domains. Lee *et al.* argue that

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this process must have dramatic effects in how ferroelectric switching proceeds in this material, as nucleation of reversed domains is not followed by growth, which should yield very large coercive fields, as is indeed observed. Interestingly, the possibility of individual switching of 2D polar planes offers the possibility of multilevel polarization switching with ideally as many intermediate states as number of unit cells. This capability is of much interest for adaptable electronics and brain-inspired computing applications.

In summary, Lee *et al.* have found that a flat phonon band gives rise to dipolar localization, a phenomenon reminiscent of localization effects in for electrons, photons, and other particles, but whose implications in the case of ferroelectrics have not been fully explored. In this way, dipolar order can occur without the need for cooperative 3D behavior, allowing miniaturization and multi-valued non-volatile storage. The next steps will be to use this knowledge to engineer lower switching voltages for memory applications in this material that is already compatible with silicon electronics.

domains to form with no energy cost.

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Figure caption: Sketch of a thin layer of (a) ferroelectric hafnia (HfO₂) and (b) a typical ferroelectric, with the blue arrows representing ferroelectric dipoles along the crystal z-direction, normal to the film surface. In both cases the films display alternating up-and-down domains (light and dark blue arrows) that eliminate net surface charges, preventing depolarization. However, while in (b) domain formation has an energy penalty due to the existing interaction between neighbouring dipoles in the y-direction, in (a) the localization of dipoles in layers, with the non-polar atomic layers represented by the gray “spacers”, allows